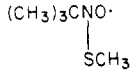
paramagnetic species of both experiments, tNB or nitrosamine as spin traps, occurred at the identical retention times and presented identical ESR spectra. Consequently, it is concluded that *tert*-butyl radicals were also generated by the photolytic cleavage of the C–S bond.

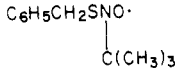
Photolysis of dimethyl disulfide in the presence of tNB in benzene solution gave the ESR spectrum shown in Figure 2. The intense triplet was attributed to radical III. A weaker set of lines was also observed (labeled C in Figure 2) with $A_N = 1.88 \pm 0.02$ mT and $A_{CH_3} = 0.08 \pm 0.02$ mT, which was attributed to radical IV, resulting from S–S bond cleavage in the photolysis of dimethyl disulfide.



IV

The spectral intensity increases at higher field due to continuous illumination and growth of radical III during the scan. In addition $M_I = 0$ and -1 peaks of both radicals overlap. Consequently, ^{13}C lines of radical III severely interfere with radical IV. The ESR spectral parameters of radical IV were reported by Wargon and Williams[13] as $A_N = 1.89$ mT and $A_{CH_3} = 0.12$ mT in their low-temperature (−103 °C) radiolysis of alkanethiol, using tNB as the spin trap.

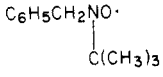
For dibenzyl disulfide, a triplet spectrum with $A_N = 1.72$ mT and $g = 2.0068$ was observed, due presumably to radical V, arising from S–S bond cleavage. Since this



V

radical has not been reported in the literature thus far, it was compared with the ESR parameters for $(CH_3)_3CN(O\cdot)SCH(CH_3)_2$ reported by Wargon and Williams[13] ($A_N = 1.699$ mT, $g = 2.0068$) and by Leaver and Ramsay[14] ($A_N = 1.67$ mT and $g = 2.0062$).

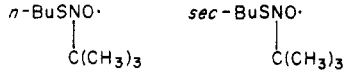
Another set of lines with $A_N = 1.50 \pm 0.02$ mT and $A_{CH_2} = 0.75 \pm 0.02$ mT and $g = 2.0062$ was also observed, which was assigned to radical VI, arising from C–S bond cleavage.



VI

Radical VI is the H adduct of α-phenyl-*N*-*tert*-butylnitrone (PBN); the ESR parameters for VI have been reported by Leaver and Ramsay[14] ($A_N = 1.498$ mT, $A_{CH_2} = 0.727$ mT, $g = 2.0062$) and several others (Mao and Kevan,[21] Mao and Kevan,[22] and Janzen and Blackburn[23]). Hence there is less uncertainty about this structure assignment.

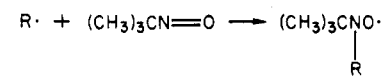
Lastly, di-*n*-butyl and di-*sec*-butyl disulfides yielded triplets ($A_N = 1.81 \pm 0.02$ mT and $A_N = 1.72 \pm 0.02$ mT, respectively), presumably due to radicals VII and VIII.



VII VIII

Discussion

We have utilized the spin-trapping technique to observe alkoxy, alkyl, and thiyl radicals simultaneously in the photodecomposition of various disulfides. In our present work, both S–S and C–S bond cleavage were observed by spin trapping the radicals generated in the photolysis of alkyl disulfides in the presence of tNB.



For di-*tert*-butyl disulfides, depending on the duration of UV irradiation, *tert*-butyl, alkoxy, and thiyl radicals were trapped. The hyperfine parameters of all four spin adducts (III, IV, V, and VI) agree well with the previously published results even though their methods of generation are quite different. We have also demonstrated that di-*tert*-butyl nitroxide radical (III) can be obtained simply by the recombination of phytolytic fragments of C–S bond cleavage from disulfides and N–N bond cleavage from nitrosamines. Unlike the tNB spin trap, nitrosamine does not contain *tert*-butyl functional group and thus di-*tert*-butyl nitroxide radical (III) must necessarily contain fragments of C–S bond breakage from disulfide molecule. The HPLC–ESR analysis further strengthened the identification of di-*tert*-butyl nitroxide radical. Di-*n*-butyl, di-*sec*-butyl, and dimethyl disulfides gave spin adducts consisting of only the S–S bond fragments, while di-*tert*-butyl and dibenzyl disulfide spin adducts indicated the trapping of both S–S and C–S bond scission products.

In summary, as most biological systems and food components contain disulfide linkages, spin-trapping techniques can be used to study their photodecomposition products since alkyl, alkoxy, and thiyl radical spin adducts give distinct ESR spectra and may be detected simultaneously.

Acknowledgment. Many helpful discussions with Dr. A. E. Pohland are deeply appreciated.

Registry No. I, 78109-57-6; II, 52323-95-2; III, 2406-25-9; IV, 58921-64-5; V, 74928-99-7; VI, 24293-08-1; VII, 58921-68-9; VIII, 78109-58-7.

Total Synthesis of the Alleged (±)-Chiloscyphone

Jean-Louis Gras

Laboratoire associé au CNRS No. 109, Université d'Aix, Marseille III, 13397 Marseille, Cedex 13, France

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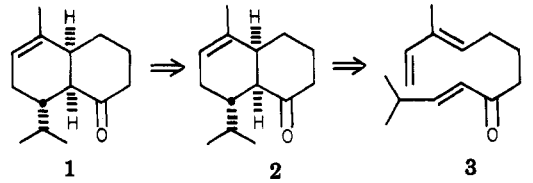
Chiloscyphone is a main component of the essential oil collected from the plant *Chiloscyphus polyanthus* (L) corda, hepaticae.[1] The structural assignment of chiloscyphone, based on its spectral properties and products derived from hydrogenation, led to the formulation 1. In this paper we describe a total synthesis of 1 by a stereospecific route, the key intermediates of which were derived by antithetic analysis (Scheme I).

Owing to the relative instability of α-methylene ketones, our initial focus was on the synthesis of octalone 2. It was envisioned that 2 could in turn be prepared via the intramolecular variant of the Diels–Alder reaction,[2] thereby forming the two six-membered rings with the simultaneous introduction of the three requisite chiral centers.[3] Accordingly, the stereospecific construction of the requisite

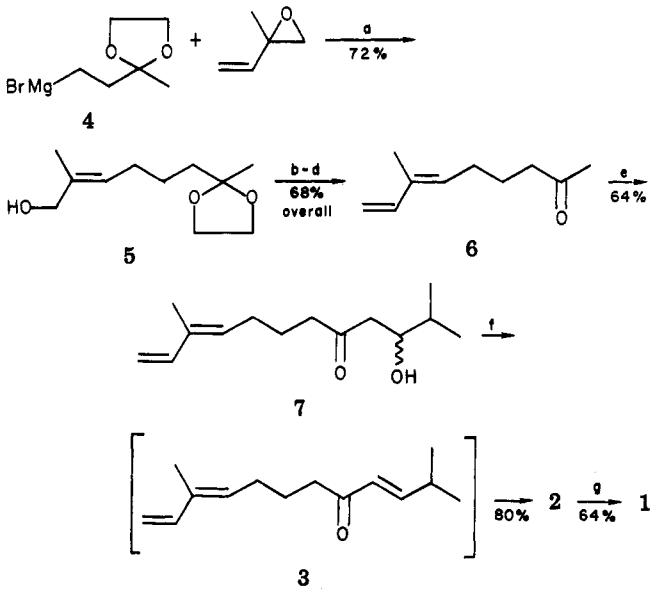
(1) Hayashi, S., Matsuo, A.; Matsuura, T. *Tetrahedron Lett.* **1969**, 1599. Matsuo, A., Hayashi, S. *Ibid.* **1970**, 1289.
(2) Oppolzer, W., *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10. Brieger, G.; Bennet, J. N. *Chem. Rev.* **1980**, *80*, 63.
(3) Gras, J.-L.; Bertrand, M. *Tetrahedron Lett.* **1979**, 4549. Taber, D. F.; Saleh, S. A. *J. am. Chem. Soc.* **1980**, *102*, 5085.

0022-3263/81/1946-3738$01.25/0

Scheme I



Scheme II[a]



[a] (a) 10% CuI, THF, −25 °C; (b) PCC, CH_2Cl_2, 15 °C; (c) Ph_3PCH_3I, *n*-BuLi, THF, 0 °C, 0.5 h; (d) 10% HCl–THF (1:4 v/v), 10 °C; (e) *i*-Bu(SiMe$_3$)$_2$COH, *n*-BuLi, isobutyraldehyde, THF, −40 to −20 °C; (f) *p*-TsOH, PhH, 42 °C, 1 h; (g) $CF_3COO^-\cdot CH_3N^+H_2$-Ph, $(CH_2O)_n$, THF, 3 h, reflux.

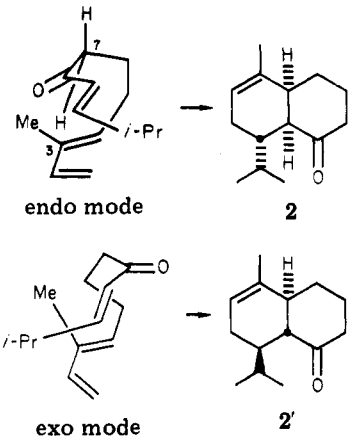
diene **3** was undertaken (Scheme II).

Copper iodide catalyzed addition of Grignard reagent **4**[4] to isoprene oxide[5] occured regioselectively at the δ carbon to give chain-extended allylic carbinol **5** in 72% yield.[6] The *E* substitution pattern at the newly formed double bond in **5** was confirmed by ^{1}H NMR analysis.[7] The allylic alcohol **5** was then oxidized with 2 equiv of pyridinium chlorochromate in methylene chloride.[8] The resulting crude α,β-unsaturated aldehyde without further purification was subjected to a Wittig reaction with methylenetriphenylphosphorane (2.5 equiv). Hydrolysis of the ketal group generated the keto diene **6** in 68% overall yield from **5** after chromatography (SiO_2, 10% ether/pentane). The trans-substituted dienophylic unit was then introduced via regioselective aldol condensation as follows. The kinetically controlled enolate formation from **6** and lithium 1,1-bis(trimethylsilyl)-3-methylbutoxide[9] was condensed with isobutyraldehyde at −20 °C in THF to afford the β-ketol **7** in 64% yield. Dehydration of **7** with *p*-toluenesulfonic acid in benzene led to enone **3** which was not isolated but readily cyclized under the experimental conditions to give octalone **2** in 80% isolated yield.[10]

Table I. 250-MHz ^{1}H NMR (δ) Features in Isomers **2** and **2a**, ppm, CCl_4

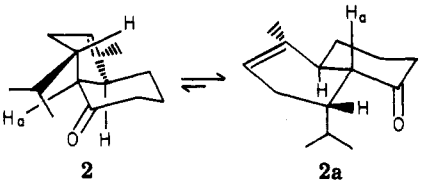
cis-octalone **2**	*trans*-octalone **2a**
2.10–2.50 (m, 3 H)	2.40–2.62 (m, 1 H) 2.10–2.28 (m, 2 H)
2.34 (dd, H_a, J = 5.3, 9.8 Hz, W_h = 18 Hz)	2.36 (dd, H_a, J = 5.8, 12 Hz, W_h = 22 Hz)
0.91 (d, J = 7 Hz), 0.81 (d, J = 7 Hz), both for *i*-Pr	0.83 (d, J = 7 Hz), 0.80 (d, J = 7 Hz), both for *i*-Pr

The stereochemical assignment in **2** resulted from a conventional application of the intramolecular Diels–Alder reaction leading to a *cis*-octalin system via an endo transition state.[3] The endo mode may present a steric repulsion between the hydrogen atom at C7 and the methyl substituent on the diene at C3. But this effect would be overriden by the steric repulsion present in the exo mode between the isopropyl substituent on the dienophile and the diene.



The equatorial orientation of the isopropyl group in **2** precludes facile epimerization to **2a** under the reaction conditions which were employed.

That **2** was indeed the kinetic product was demonstrated by isomerization of **2** under forcing conditions (e.g., NaH, Me_2SO, 22 °C, 4 days or H_2SO_4–AcOH, 22 °C, 6 days, 24% yield) after an uphill conformational change to give the epimer **2a** in which the isopropyl group is now axially oriented.



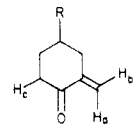
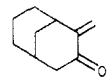
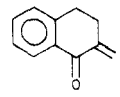
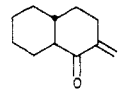
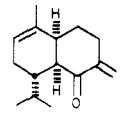
14:86

The two epimers, **2** and **2a**, had similar but not identical IR and ^{1}H NMR spectra.[11] The two ^{1}H NMR (250 MHz) spectra indicated a better resolution of the protons α of the carbonyl group and at the ring fusion in isomer **2a** and a greater difference between the chemical shifts of the 2-methyl groups of the *i*-Pr substituent in isomer **2** (Table I).

(4) Ponaras, A. A. *Tetrahedron Lett.* **1976**, 3105. Büchi, G.; Wüest, H. *J. Org. Chem.* **1969**, *34*, 1122.
(5) Reist, E. J.; Junga, I. G.; Baker, B. R. *J. Org. Chem.* **1960**, *25*, 1673.
(6) Cahiez, C.; Alexakis, A.; Normant, J. F. *Synthesis* **1978**, 528.
(7) Corey, E. J.; Yamamoto, H. *J. Am. Chem. Soc.* **1970**, *92*, 226. Prisbylla, M. P.; Takabe, K.; White, J. D. *Ibid.* **1979**, *101*, 762. Taylor, W. G.; Coutts, R. T. *Can. J. Chem.* **1979**, *57*, 2103.
(8) Corey, E. J.; Sugg, W. J. *Tetrahedron Lett.* **1975**, 2647.
(9) Kuwajima, I.; Sato, T.; Arai, M.; Minami, N. *Tetrahedron Lett.* **1976**, 1817.

(10) Isolation of a mixture containing enone **3** before completion of the dehydration showed a coupling constant between the two newly introduced vinylic protons of J = 16 Hz. This ensured a trans arrangement of the dienophile unit.
(11) Octalone **2a**: IR (neat) 3038, 1705, 1642 cm^{-1}; NMR (CCl_4) δ 5.32 (br s, 1 H), 2.36 (dd, 1 H, J = 5.8, 12 Hz), 2.40–2.62 (m, 1 H), 2.10–2.28 (m, 2 H), 1.98 (m, 4 H), 1.66 (s, 3 H), 1.46–1.86 (m, 3 H), 1.52 (m, 1 H), 0.83 (d, 3 H, J = 7 Hz), 0.80 (d, J = 7 Hz, 3 H).

Table II. Spectroscopic Data of Some α-Methylenecyclohexanones, Synthetic Material, and Natural Chiloscyphone

	IR (CCl_4)		NMR ($CDCl_3$)	
	$\nu_{C=O}$, cm^{-1}	$\nu_{C=O}/\nu_{C=C}$[14]	δ_{H_c}	$\delta_{H_a} - \delta_{H_b}$
 R = H	1690	1.5	2.2	0.7
R = t-Bu	1690	1.5	2.25	0.92
	1692	2.4	2.6	0.64
	1695	1.8	2.22	0.66
	1688	1.4	2.2	0.92
	1713	2.8	2.69	0.95
	1680	2.3		0.83
	1698	2.3	2.6	0.62
 CCl_4	1694	2.6	2.4	0.6
$CDCl_3$	1685			
synthetic chiloscyphone (neat)	1670	6.0	3.59	0.21

Finally, an exo transition state would afford 2′ with a trans ring fusion and an equatorially oriented isopropyl group. This most stable structure would probably not be epimerized.

For completion of the synthesis, octalone 2, with its three chiral centers in the required relative configuration, was subjected to α-methylenation. In this instance, application of the recently developed direct α-methylene transfer was possible.[12] Thus, treatment of 2 with *N*-methylanilinium trifluoroacetate and paraformaldehyde afforded the desired α-methylenated product 1 in 64% yield (70% conversion).

The IR and ^1H NMR spectra of synthetic 1 were in complete accord with the target structure 1; however, these proved to be distinctly different from those of the natural product.[13] After comparison with different α-methylene cyclohexanones, it can be concluded that chiloscyphone does not belong to this class of compounds. The most striking differences in spectroscopic properties are indicated in Table II.

The synthetic material proved to be relatively unstable and as an α-methylene ketone did not lead to any hydrazone, although the natural product did. Since the structure of our synthetic compound 1 is assured both by its unambigous method of synthesis as well as by its spectral data, we must conclude that the structure originally assigned to chiloscyphone is in error.

(12) Gras, J.-L. *Tetrahedron Lett.* **1978**, 2111.

(13) The possibility that a difference in stereochemistry was responsible for the variations in spectral properties was ruled out by recovery of unchanged octalone 2 after partial α-methylenation.

(14) This ratio lies between 0.6 and 3.5 for cisoidal enones and is greater than 6 for transoidal enones: Mecke, R.; Noak, A. *Chem. Ber.* **1960**, *93*, 210. Erskine, R. L.; Waight, E. S. *J. Chem. Soc.* **1960**, 3425.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 267 spectrophotometer. ^1H nuclear magnetic resonance were taken on a Varian EM 360 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained by using a Varian MAT 111 instrument (80 eV). Microanalyses were performed in the analytical section of our department. Solvents were distilled from sodium benzophenone ketyl. All reactions were carried out under a nitrogen atmosphere. Merck silica gel 60 (70–230 mesh) was employed for preparative chromatography.

Allylic Alcohol 5. A mixture of 2-(2-bromoethyl)-2-methyl-1,3-dioxolane (6.435 g, 33 mmol) and 1,2-dibromoethane (0.104 mL, 1.2 mmol) in 7.5 mL of THF was added over 5 min to a suspension of powdered magnesium (0.864 g, 36 mmol) in 7.5 mL of THF. After the reaction was initiated, it was maintained for 1 h at 5 °C and then diluted with 10 mL of THF. The resulting mixture was added over a 20-min period to a mixture of isoprene oxide (2.52 g, 30 mmol) and copper iodide (0.57 g, 3 mmol) in THF (10 mL) cooled to −25 °C. After 1 h more, the reaction was quenched with NH_4Cl solution (25 mL) and extracted with Et_2O. The organic layers were washed with a 3% NH_4OH solution (60 mL) and water and dried over magnesium sulfate. Rapid chromatographic purification afforded 4.32 g of alcohol 5: IR (neat) 3400, 1640, 1050 cm^{-1}; NMR (CCl_4) 5.33 (t, J = 7 Hz, 1 H), 3.82 (s, 4 H), 3.43 (br s, 2 H), 3.10 (s, 1 H), 2.02 (m, 2 H), 1.8–1.2 (m, 4 H), 1.63 (s, 3 H), 1.23 (s, 3 H) ppm.

Diene Ketone 6. Pyridinium chlorochromate (4.3 g, 20 mmol) was suspended in 30 mL of anhydrous CH_2Cl_2 cooled to 15 °C. A solution of carbinol 5 (2 g, 10 mmol) and 10 mL of CH_2Cl_2 was quickly added, and the mixture was stirred at room temperature for 1 h. The mixture was filtered through Celite, and the solid residue was washed thoroughly with dry ether. Concentration under vacuum afforded 2.12 g of crude liquid aldehyde: IR (neat) 2715, 1690, 1645, 1050 cm^{-1}; NMR (CCl_4) 9.2 (s, 1 H), 6.27 (t, J = 7 Hz, 1 H), 3.76 (s, 4 H), 2.32 (m, 2 H), 1.77 (s, 3 H), 1.9–1.3 (m, 4 H), 1.26 (s, 3 H) ppm.

Methyltriphenylphosphonium iodide (10.1 g, 25 mmol) and anhydrous THF (40 mL) were refluxed for 0.5 h under Ar. The heterogeneous mixture was cooled to 0 °C, and 12.5 mL of a 2 M *n*-BuLi solution in hexane was quickly added. After the mixture was stirred 1 h at 0 °C, the crude aldehyde in 10 mL of THF was added over a 10-min period. The mixture was hydrolyzed after 0.5 h, extracted with pentane, washed with a 3% HCl solution, and concentrated for use as such for the next step: IR (neat) 3080, 1642, 1608, 1060, 890 cm^{-1}; NMR (CCl_4) 6.27 (dd, J = 18, 11 Hz, 1 H), 5.46 (t, J = 7 Hz, 1 H), 5.06 (m, 1 H), 4.82 (m, 1 H), 3.80 (s, 4 H), 2.06 (m, 2 H), 1.70 (s, 3 H), 1.48 (m, 4 H), 1.18 (s, 3 H) ppm.

A solution of the diene ketal in 20 mL of THF was treated with 5 mL of a 10% HCl solution at room temperature for 1 h. Then, the solution was diluted with 20 mL of pentane, washed with a saturated $NaHCO_3$ solution, and dried over $MgSO_4$. Chromatographic purification (SiO_2) afforded 1.03 g (68% overall yield from 5) of diene ketone 6: IR (neat) 3080, 3030, 1720, 1640, 1608, 895 cm^{-1}; NMR (CCl_4) 6.32 (dd, J = 17, 11 Hz, 1 H), 5.42 (t, J = 7 Hz, 1 H), 5.06 (d, J = 17 Hz, 1 H), 4.91 (d, J = 11 Hz, 1 H), 2.62–2.0 (m, 4 H), 2.12 (s, 3 H), 1.76 (s, 3 H), 1.91–1.5 (m, 2 H) ppm; mass spectrum, m/e 152 (M^+), 143, 109, 94, 79, 69, 43, 41. Anal. Calcd for $C_{10}H_{16}O$: C, 120.11; H, 16.13. Found; C, 120.18; H, 16.27.

β-Ketol 7. Lithium 1,1-bis(trimethylsilyl)-3-methylbutoxide was prepared by treating the corresponding alcohol (2.506 g, 10.8 mmol) in 13.5 mL of THF with *n*-BuLi (5.4 mL, 10.8 mmol) at −20 °C for 20 min. Methyl ketone 6 (1.368 g, 9 mmol) in THF (7 mL) was then added in 10 min at −40 °C, followed by freshly distilled isobutyraldehyde (0.980 mL, 10.8 mmol) in 7 mL of THF. After the resulting solution was stirred for 4 h at −20 °C, it was quenched with aqueous NH_4Cl and extracted with Et_2O. Removal of the solvent and filtration through a short silica gel column afforded 1.290 g (64% yield) of β-ketol 7: IR (neat) 3450, 3090,

3040, 1710, 1646, 1612, 895 cm^{-1}; NMR (CCl_4) 6.33 (dd, J = 17, 11 Hz, 1 H), 5.43 (t, J = 7 Hz, 1 H), 5.03 (d, J = 17 Hz, 1 H), 4.93 (d, J = 11 Hz, 1 H), 3.73 (q, J = 6 Hz, 1 H), 3.13 (s, 1 H), 2.43 (d, J = 6 Hz, 2 H), 2.55–1.25 (m, 7 H), 1.73 (s, 3 H), 0.90 (d, J = 8 Hz, 6 H) ppm.

***cis*-Octalone 2.** A solution of ketol **7** (1.120 g, 5 mmol) and *p*-TsOH (86 mg, 0.5 mmol) in benzene (12.5 mL) was heated to 42 °C. After 1 h the solution was diluted with Et_2O (30 mL), washed with aqueous $NaHCO_3$, and dried. Purification on silica gel afforded 865 mg (84% yield) of *cis*-octalone **2**: IR (neat) 3035, 1709, 1630 cm^{-1}; ^1H NMR (CCl_4) 5.34 (br s, 1 H), 2.34 (dd, 1 H, J = 5.3, 9.8 Hz), 2.1–2.5 (m, 3 H), 1.88–2.08 (m, 4 H), 1.54–1.88 (m, 4 H), 1.66 (s, 3 H), 1.48 (m, 1 H), 0.91 (d, 3 H, J = 7 Hz), 0.81 (d, 3 H, J = 7 Hz) ppm; ^{13}C NMR ($CDCl_3$) 214 (s), 135.5 (s), 121.6 (d), 54.5 (d), 44.2 (d), 39.8 (t), 36.5 (d), 28.5 (d), 27.3 (t), 26.1 (t), 24.3 (t), 21.8 (q), 21.2 (q), 15.5 (q) ppm; mass spectrum, m/e 206 (M^+), 191, 163, 149, 124, 55, 43, 41. Anal. Calcd for $C_{14}H_{22}O$: C, 168.15; H, 22.18. Found: C, 168.23; H, 22.29.

α-Methylene Ketone 1. A mixture of paraformaldehyde (180 mg, 6 mmol) and *N*-methylanilinium trifluoroacetate (284 mg, 4 mmol) in 3 mL of THF was refluxed for 20 min. *cis*-Octalone **2** (206 mg, 1 mmol) was added and the resulting solution was refluxed 3 h more. After cooling, the reaction mixture was diluted with Et_2O (20 mL) and hydrolyzed with 20 mL of half-saturated $NaHCO_3$ solution. The crude product was extracted with Et_2O and dried. Purification on a silica gel column afforded 140 mg of α-methylene ketone **1** (64% yield) along with 61 mg of recovered octalone **2**: IR (neat) 3090, 3040, 1693, 1620, 932 cm^{-1}; area $\nu_{C=O}$/area $\nu_{C=C}$ = 2.6;[14] NMR ($CDCl_3$) 5.59 (m, 1 H, methylenic), 5.36 (m, 1 H, vinylic), 5.0 (m, 1 H, methylenic), 2.6–2.2 (br m, 3 H), 1.90 (br m, 5 H), 1.66 (s, 3 H), 1.25 (br m, 2 H), 1.85 (br d, J = 6 Hz, 6 H) ppm.

Natural chiloscyphone (**1**): IR (neat) 1670, 1629, 935 cm^{-1}; area $\nu_{C=O}$/area $\nu_{C=C}$ = 6; NMR ($CDCl_3$) 5.96 (s, 1 H methylenic), 5.75 (d, J = 1.2, 1 H, methylenic), 5.42 (m, 1 H, vinylic), 3.59 (q, J = 6.9, 2.0 Hz, 1 H, methine), 2.53 (m, 2 H), 2.0 (m, 3H), 1.83 (d, J = 1.2 Hz, 3 H), 1.67 (m, 1 H), 1.37 (m, 3 H), 0.96 (s, 3 H), 0.85 (d, J = 5.5, 3 H).

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Registry No. 1, 78183-88-7; 2, 78109-27-0; **2a**, 78109-28-1; **4**, 37865-96-6; (*E*)-**5**, 78109-29-2; (*E*)-**6**, 78109-30-5; (*E*)-**6** ethylene glycol, 78109-31-6; (*E*)-**7**, 78109-32-7; isoprene oxide, 1838-94-4; (*E*)-6-(2-methyl-1,3-dioxol-2-yl)-2-methyl-2-hexenal, 78109-33-8; isobutyraldehyde, 78-84-2.

Efficient Synthesis of a New Nucleophilic Acetaldehyde Equivalent: (*Z*)-2-(Trimethylsiloxy)vinyllithium

Lucette Duhamel* and Francis Tombret

Laboratoire de Chimie Organique de la Faculté des Sciences et des Techniques de Rouen, 76130 Mont Saint Aignan, France

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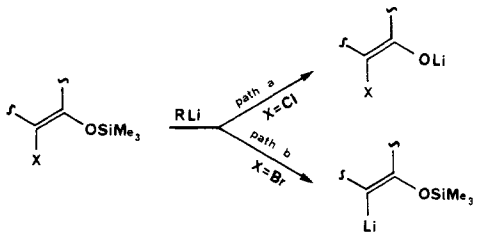
It is well-known that the trialkylsilyl enol ethers are readily cleaved by organometallic reagents.[1] Particularly, this is the case of the β-chloro(trimethylsilyl) enol ethers which are transformed into β-chloro enolates by reaction with methyllithium[2] (Scheme I, path a). We report our finding that with β-bromo(trimethylsilyl) enol ethers and *tert*-butyllithium, the selectivity of this reaction is reversed; i.e., the halogen–metal exchange reaction is faster than the oxygen–silicon cleavage (path b). Thus 2-halo(trimethylsilyl) enol ethers may be converted either to 2-halo enolates or vinyllithium reagents, depending on the halogen and reaction conditions.

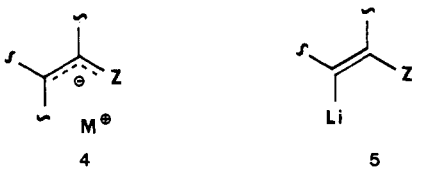
Scheme I



(*Z*)-[(Trimethylsiloxy)vinyl]lithium (**1**) is a relatively stable nucleophilic acetaldehyde equivalent (over 20 h in diethyl ether at −70 °C).

This compound is conveniently prepared (path b) by reaction of *tert*-butyllithium in diethyl ether at −70 °C with (*Z*)-2-bromo-1-(trimethylsiloxy)ethylene.[3] At low temperature, the anion **1** reacts with carbonyl compounds to produce the alcohols **2** (Scheme II), which are easily hydrolyzed into unsaturated carbonyl compounds **3** (see Table I).

In addition to ambident anions **4** (Z = NR,[4,5] $NNMe_2$,[6] O[7]), available since the pioneering work of Stork and Dowd,[4] the vinylic anions **5** (Z = OR,[8] OLi,[9] NR_2[8b,10]) constitute a new class of nucleophilic aldehyde and ketone equivalents of considerable synthetic value.



4 5

Several characteristic advantages of the new reagent **1** should be mentioned: the ease of its preparation, the availability of its precursor (*Z*)-2-bromo(trimethylsiloxy)ethylene (95% *Z*),[3] and the well-known ease of hydrolysis of the generated labile trimethylsiloxy derivatives.

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